Polyoxometalate-based gels and nanostructured materials for decontamination under ambient conditions

Craig L. Hill, Wade Neiwert, Nelya Okun, Michelle Ritorto, Travis Anderson, Huandong Zeng, Lei Zang, Chris Tarr, and Jeff Rhule

Department of Chemistry
Emory University, Atlanta, GA, USA

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **19 NOV 2003**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Polyoxometalate-based gels and nanostructuredmaterials for decontaminationunder ambient conditions**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Department of ChemistryEmory University, Atlanta, GA, USA**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM001851, Proceedings of the 2003 Joint Service Scientific Conference on Chemical & Biological Defense Research, 17-20 November 2003. , The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**20**	

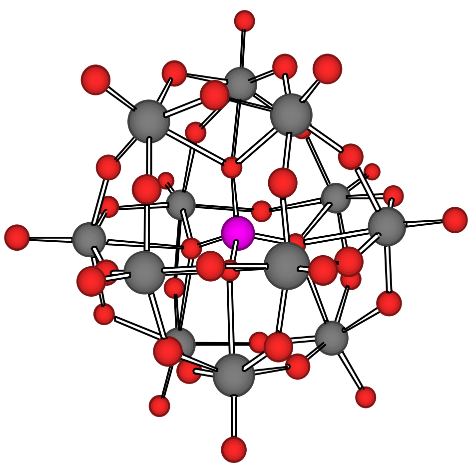
Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Abstract

Four new types of materials that all catalyze the desired oxidative decontamination (selective sulfoxidation) of CEES, the best mustard (HD) simulant, using simply air as the oxidant under extremely mild conditions will be described. The high reactivity for this challenging yet attractive decontamination/protection chemistry derives in all cases from the incorporation of particular catalytically active polyoxometalates (POMs) into the materials. First, a gel comprised of esterified hexavanadate (V_6) POM units will be described. This concept material exhibits 3 target properties: It swells with and physically traps CEES, changes color by CEES reduction of the V_6 units, and catalyzes the O_2/air oxidation of CEES. The second material comprises negatively-charged POMs electrostatically bound to cationic cellulosics. This "catalytic cotton" constitutes one attempt to render BDUs and other protective apparel catalytically self-decontaminating and thus more effective. The third material entails POMs electrostatically bound to cationic metal oxide nanoparticles. The fourth is a nanoporous material that forms by self assembly of silver cations and the heteropolyanion $PV_2Mo_{10}O_{40}^{5-}$. The preparation, characterization and catalytic properties of the materials will be summarized, and their common catalytic features will be addressed. This work was and is supported by Army Research Office.

Transition-metal oxygen anion clusters (polyoxometalates or “POMs”)

$$n\,[WO_4]^{2-} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underbrace{[W_xO_y]^{n-}}_{\text{polyoxometalates}} + nH_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underbrace{WO_3}_{\text{metal oxide}} + nH_2O$$



$[AlW_{11}O_{40}]^{6-}$ (Keggin)

Al, purple; W, gray, O, red

- **stable (O_2, H_2O)**
- **accessible**
- **scalable**
- **nontoxic**
- **inexpensive**

readily alter:

- **elemental compositions**
- **potentials**
- **acidities**
- **solubilities**
- **shape, size, charge**
- **others**
- **counterions**

extremely versatile

An interplay and interdependence of characterization methods for soluble, insoluble and nanostructured materials

Techniques for soluble species

(1) NMR (all nuclei in POMs)

(2) FTIR, Raman

(3) UV-visible

(4) Electrochemical methods

(5) mass spec (LC-MS/MS)

Techniques for solids

(1) X-ray

(2) CP/MAS NMR

(3) SEM (SEM/EDS)

(4) TEM

(5) TGA & DSC

Techniques for nanostructure

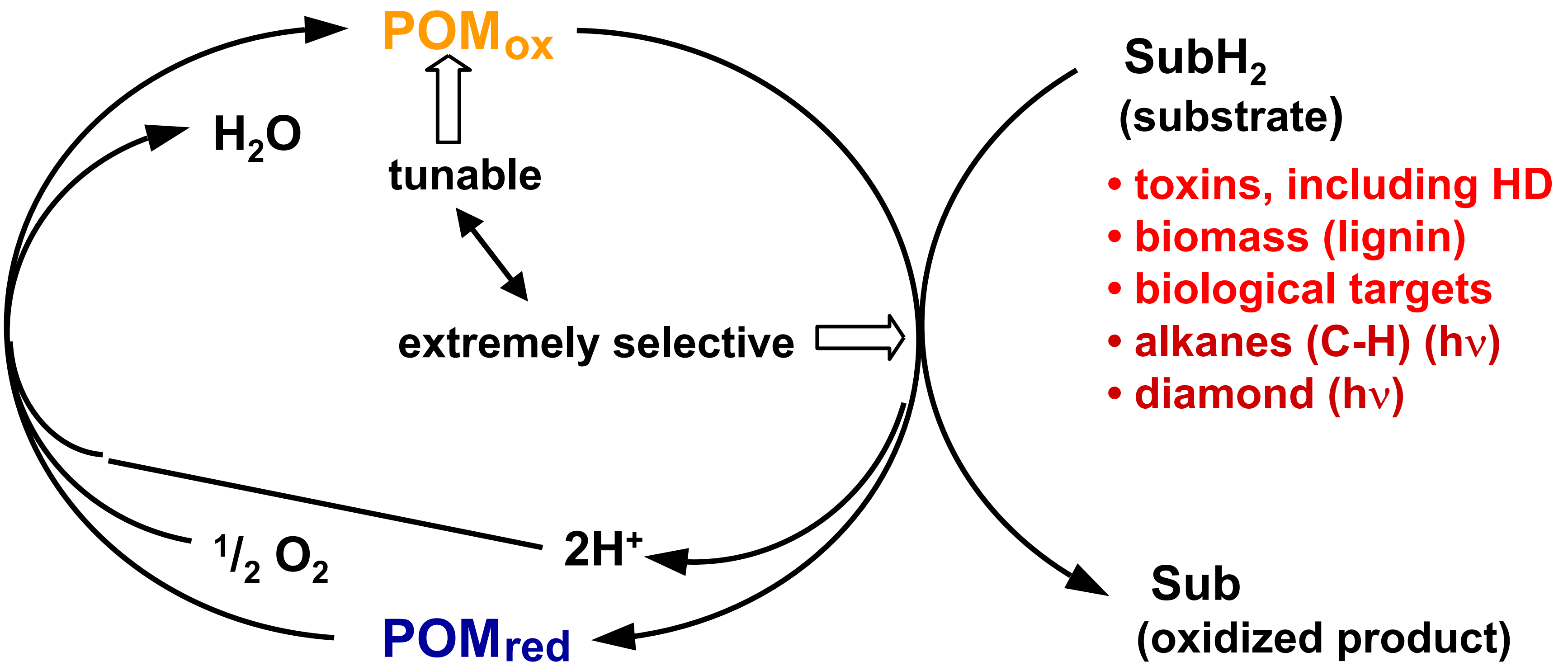
(1) STM

(2) AFM

(3) SAXS

Drs. S. Wu, K. Hardcastle, R. Apkarian, F. Strobel

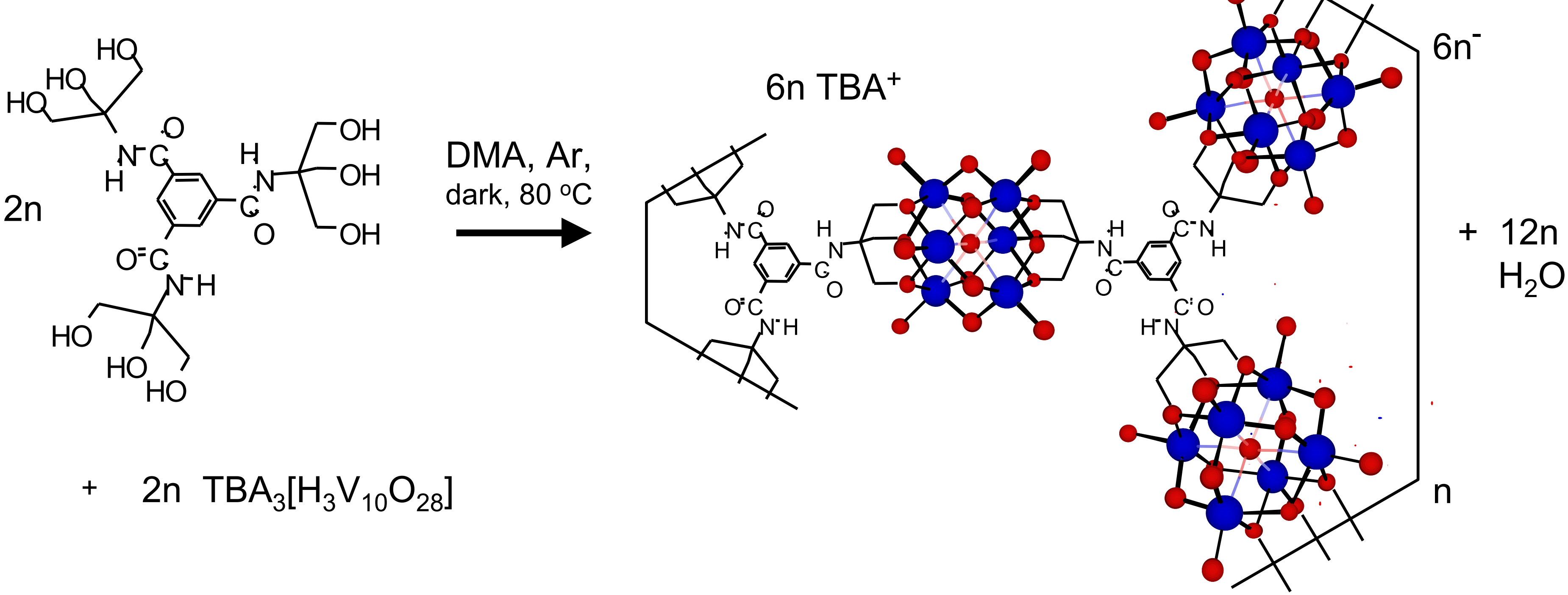
General catalytic cycle for selective O_2-based oxidation



Net rxn : $\quad SubH_2 + {}^1/_2\, O_2 \xrightarrow[\text{(catalyst)}]{POM_{ox}} Sub + H_2O$

Covalent multi-functional, nanostructured material

- **One-pot self-assembly synthesis**



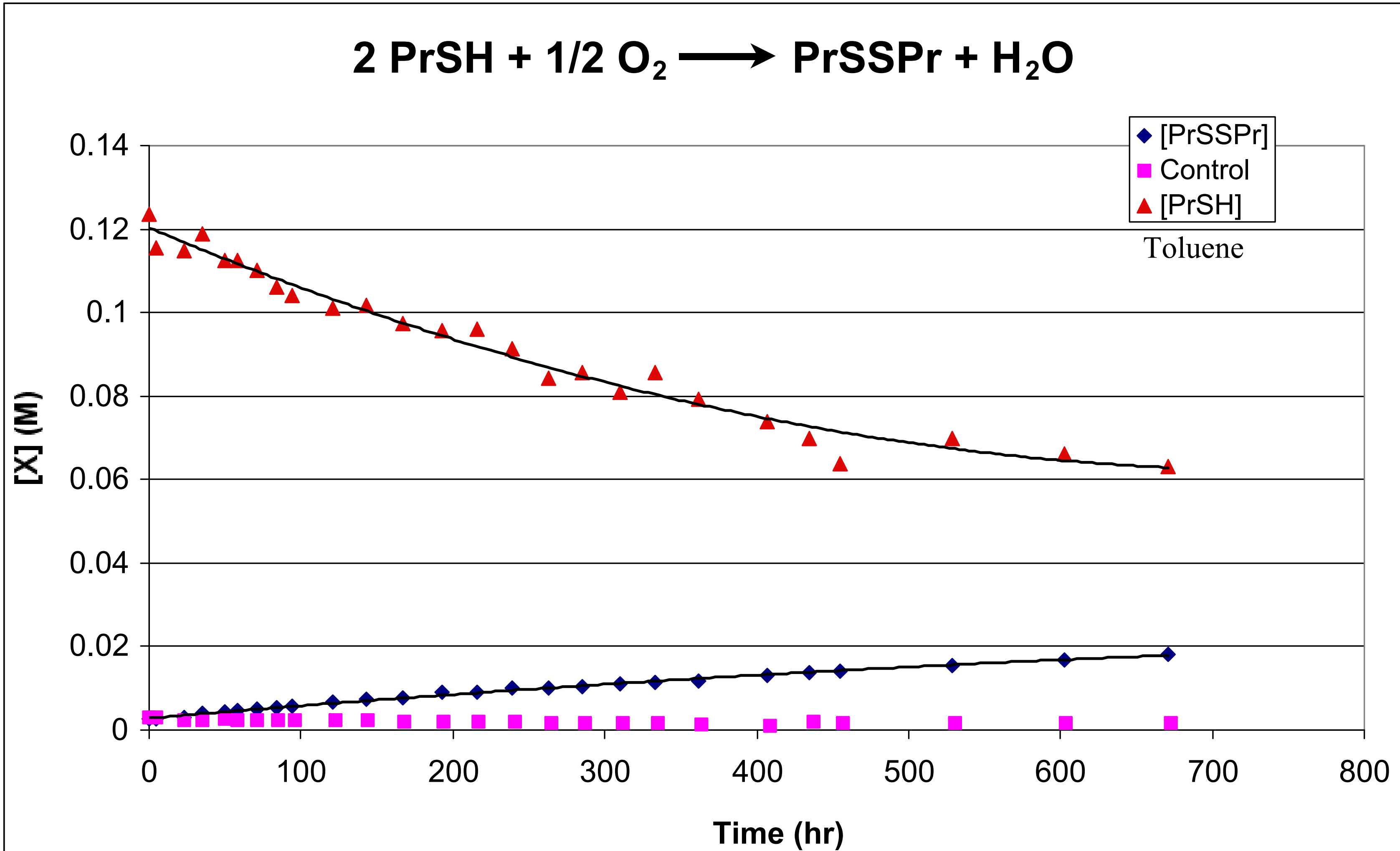
- **Recognizes, bind target (swells)**
- **Detects target (color change)**
- **Catalytically transforms target (air oxidation)**

Systematically alter:

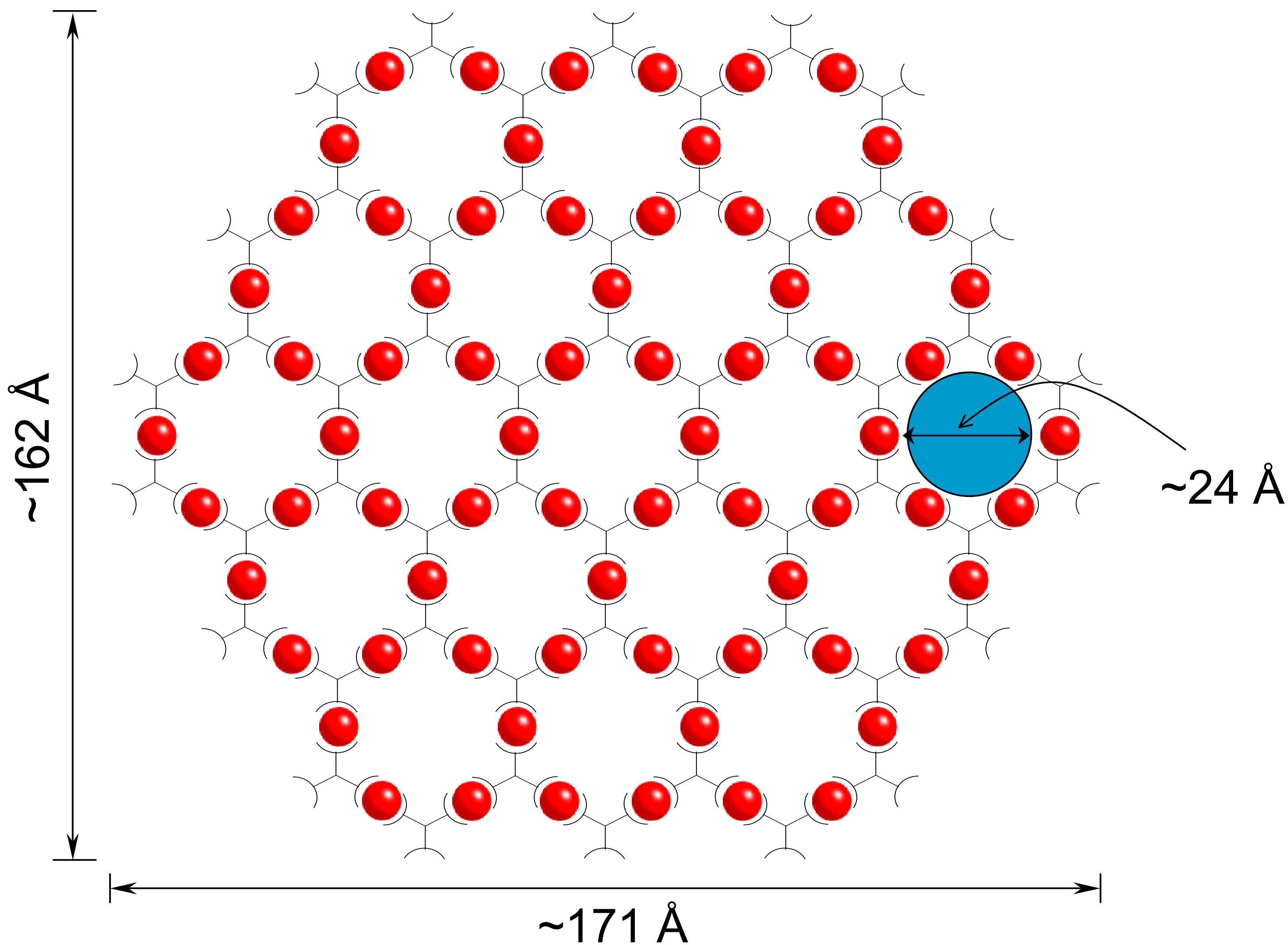
- **cluster composition, linkage sizing, counterions,**

Controls pore size, pore polarity, swellability, etc.

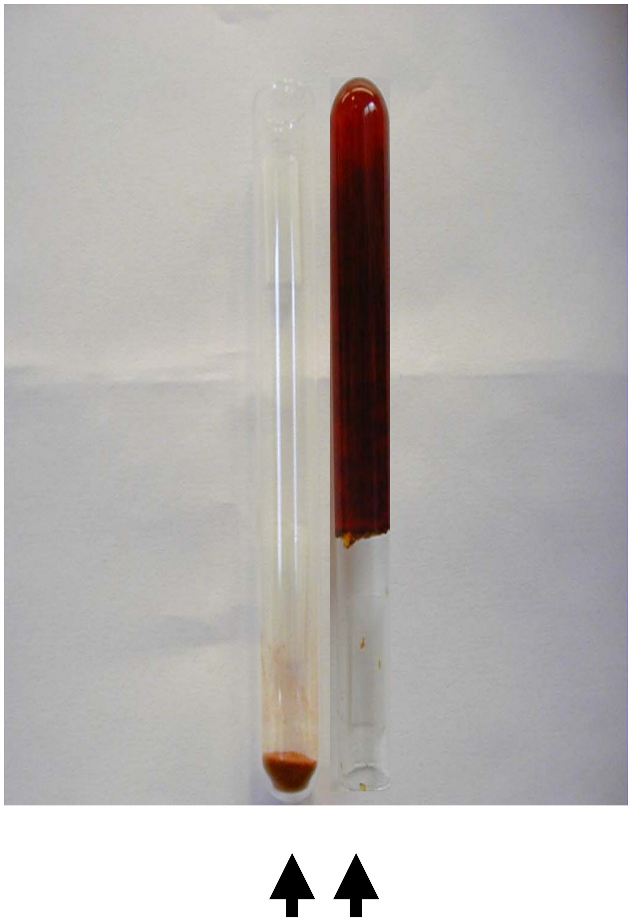
Catalysis by gel (air, 25 °C)



Small Angle X-ray Scattering (SAXS) gives Nanostructural Information Confirmed by X-ray Analysis of a Monomeric Model and Atomic Force Microscopy (AFM)

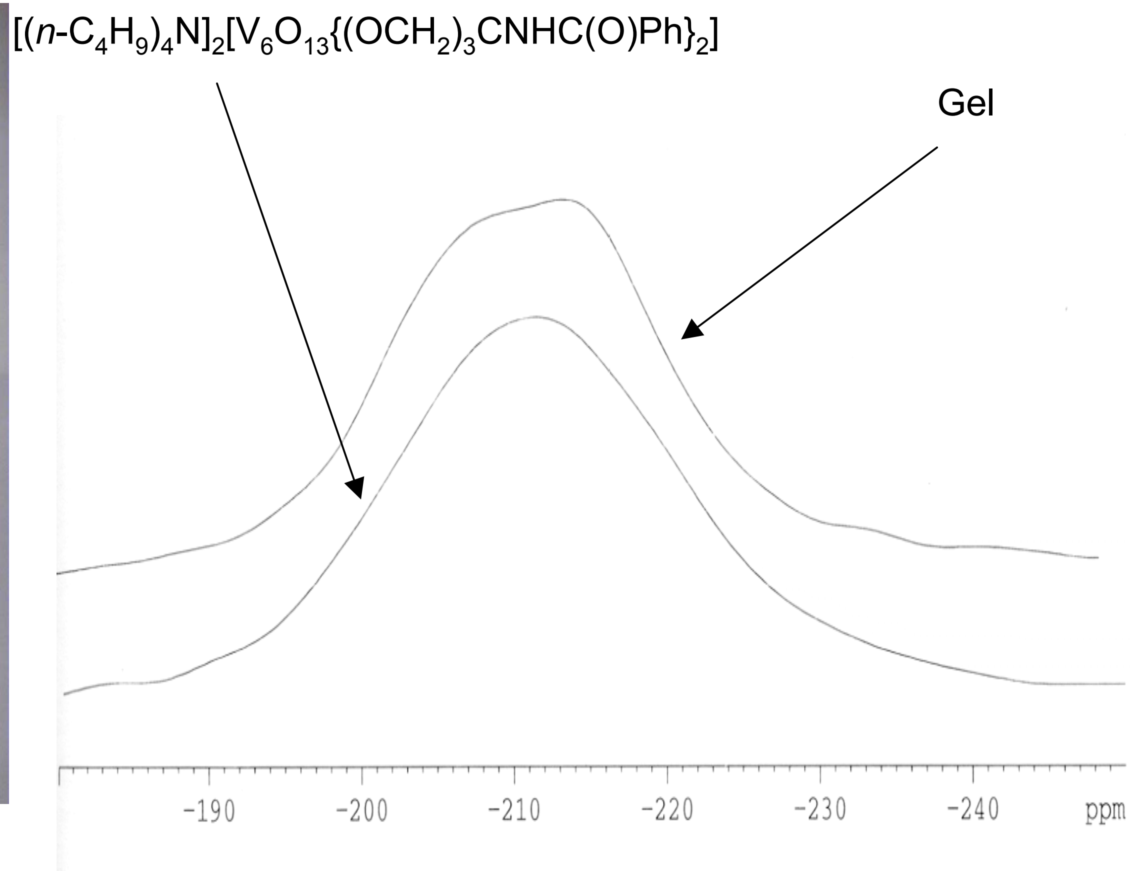


array is a gel



before & after DMF
(same sample)

^{51}V Solid-State NMR of Gel and Monomer

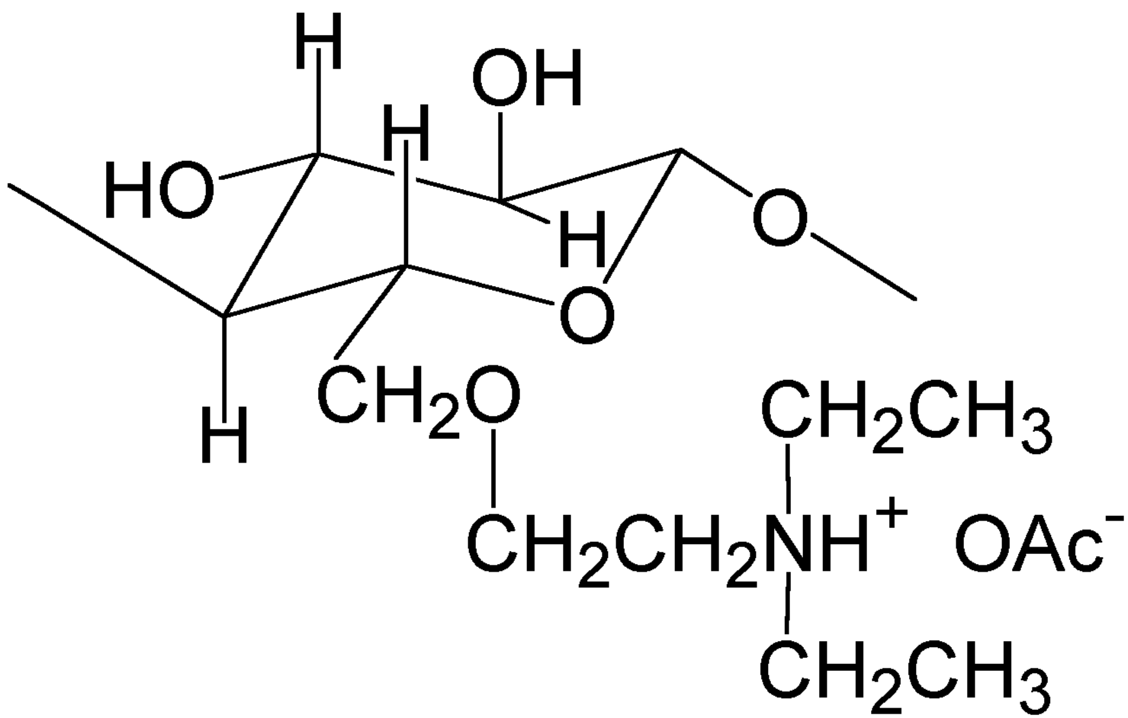


Synthesis of "Catalytic-Cotton"

Cotton Ball → 20% diethylaminoethyl chloride hydrochloride 2x → 8% NaOH 95 ºC, 10 min → Wash w/ dilute CH_3COOH → Wash w/ H_2O → Dried under ambient conditions

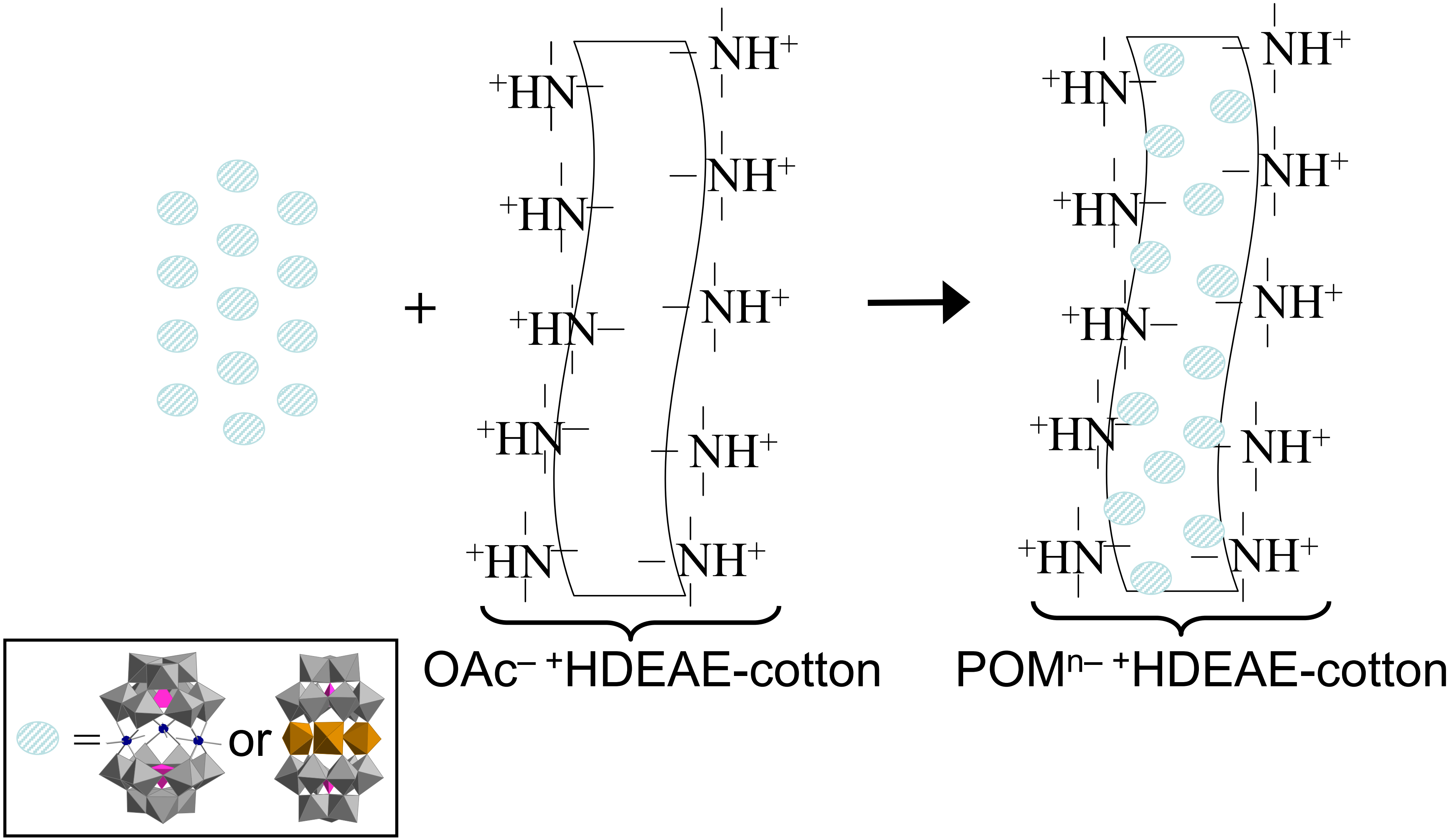
Soignet, D. M.; Benerito, R. R.; Pilkington, M. W. *Textile Res. J.* **1969**, *39*, 485-496.

Example of DEAE-Functionalized Subunit

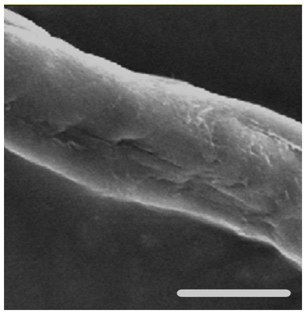


- After 2 treatments ~25% of subunits functionalized with DEAE groups

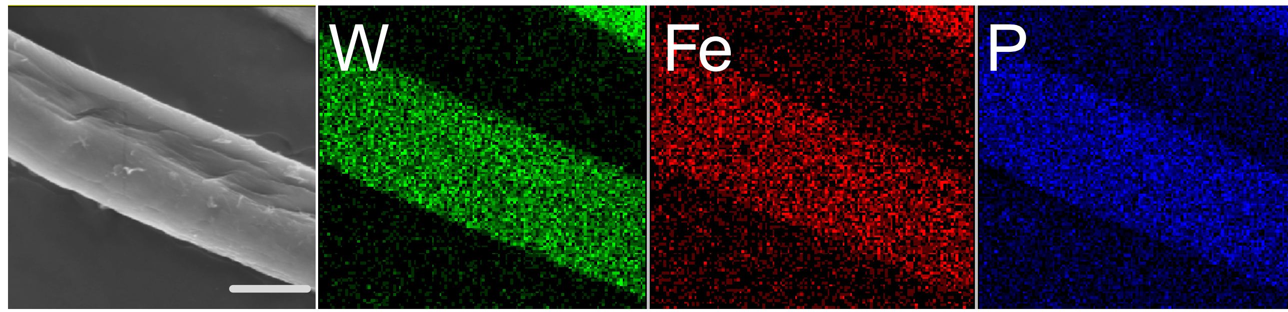
Synthesis of $POM^{n-}\ {}^{+}HDEAE$-Cottons



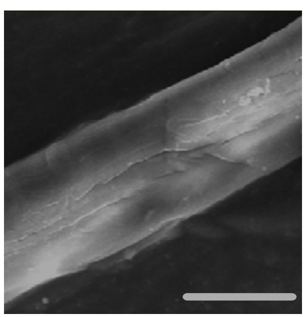
SEM-EDS



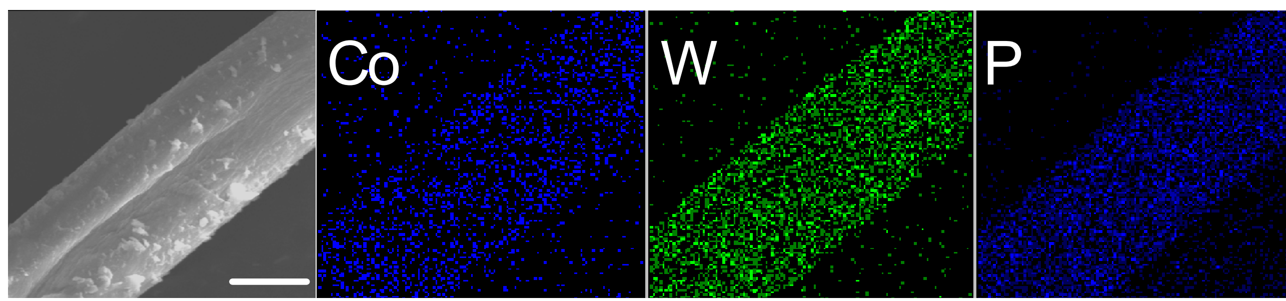
Untreated cotton



$[(Fe(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{9-}$ $^{+}$HDEAE-cotton



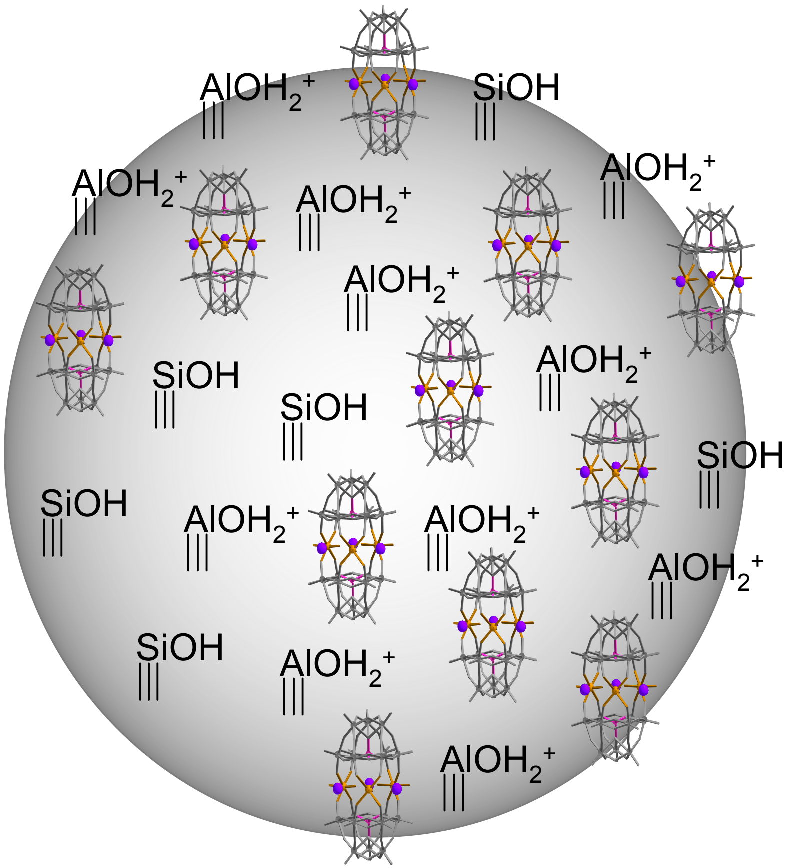
DEAE-cotton

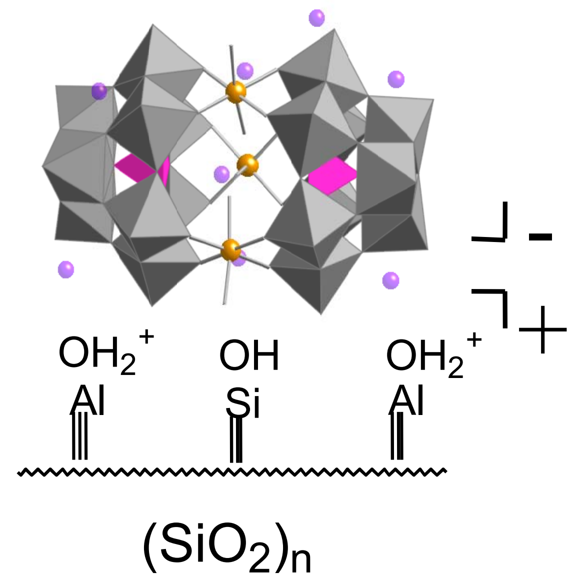


$[(Co(OH_2)_2)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$ $^{+}$HDEAE-cotton

Bar = 10 μm

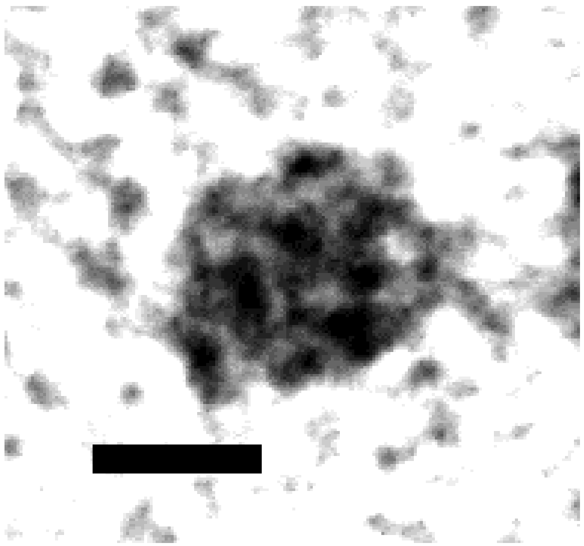
Illustration of the electrostatic association of $\{K_8[Fe_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]\}^-$ monoanions with the cationic surfaces of the $(Si/AlO_2)^{n+}$ nanoparticles



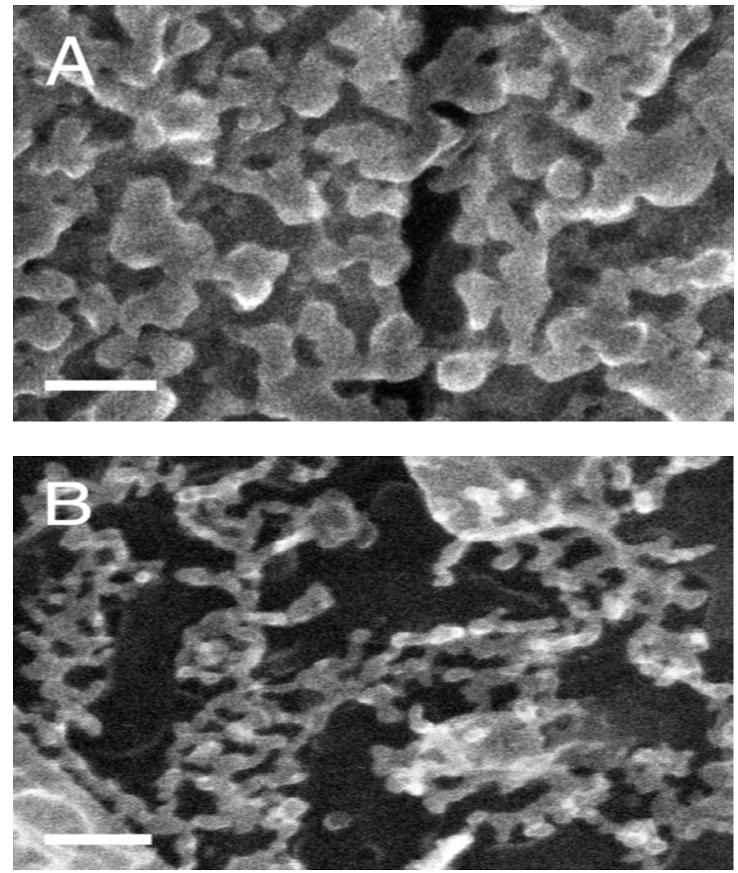


N.M. Okun, T.M. Anderson, C.L. Hill, *J. Am. Chem. Soc.* **2003**, *125*, 3194.

TEM and cryo-HRSEM



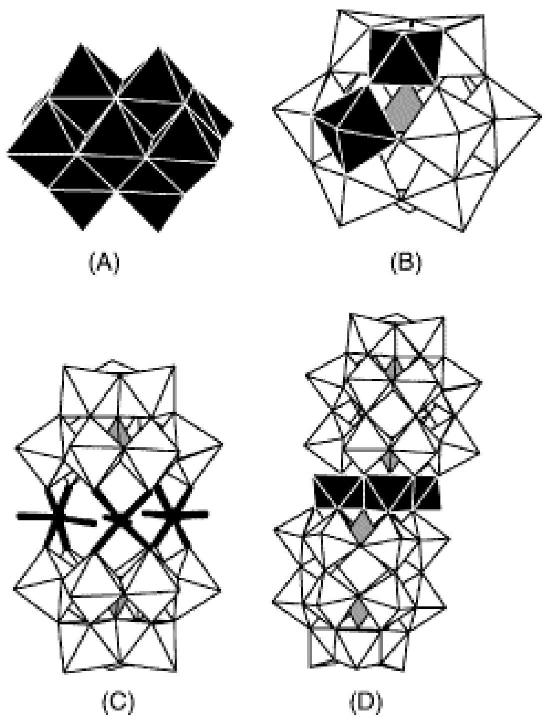
TEM image of an average-sized (~17 nm) particle of POM after catalysis. The sizing bar is 10 nm in length.
The dark spots of POM are more visible on the lighter background of the larger Si/AlO_2 nanoparticles.



Cryo-HRSEM of cationic silica ($(Si/AlO_2)Cl$) and
POM-nanoparticles. Both samples were aged 4 months prior to imaging.

Binary Cupric Nitrate/Triflate Systems

CEES + 0.5 O_2 $\rightarrow$ CEESO



1. POMs alone (solution or solid) are ineffective.

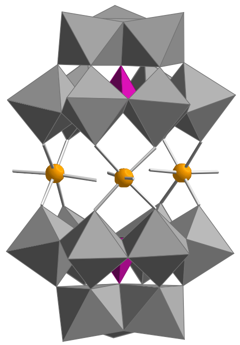
2. Binary cupric nitrate/triflate gives ~56% conversion in 24 h.

3. Binary cupric system + POMS still only gives 56% conversion.

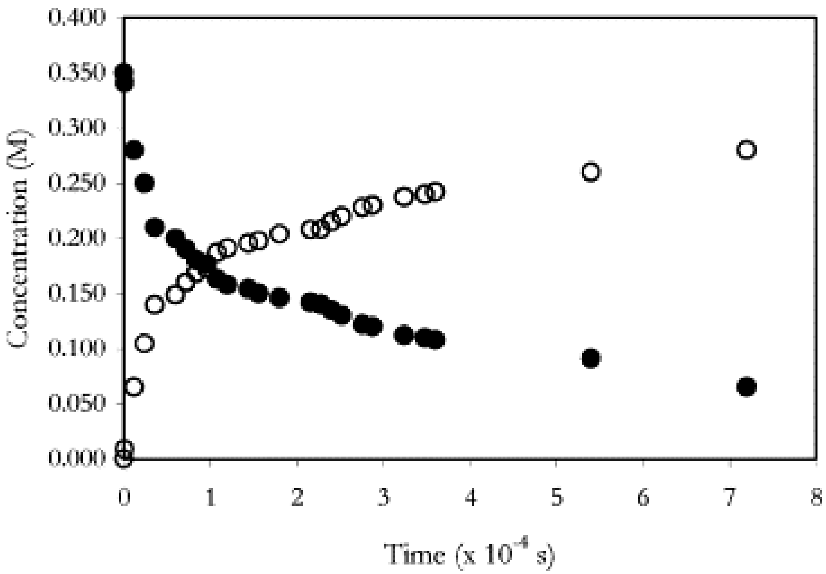
4. Binary cupric system + POMs on cationic silica is highly effective with up to 94% conversion in 24 h.

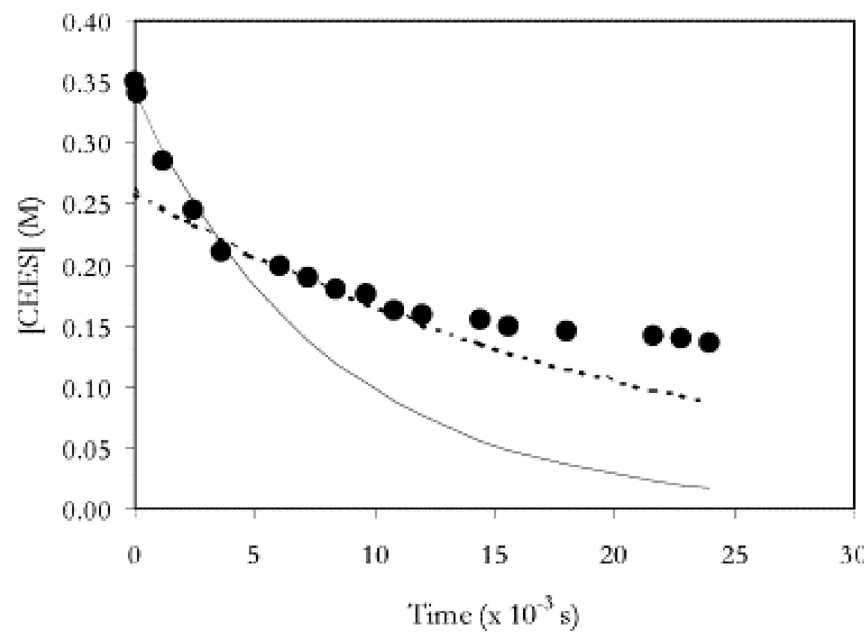
Okun, N. M.; Anderson, T. M.; Hill, C. L. *J. Mol. Catal. A: Chem.* **2003**, *197*, 283-290.

Binary Cupric Nitrate/Triflate Systems



The best catalyst was the A-type Fe(III) sandwich on cationic silica plus the binary cupric nitrate/triflate co-catalyst.



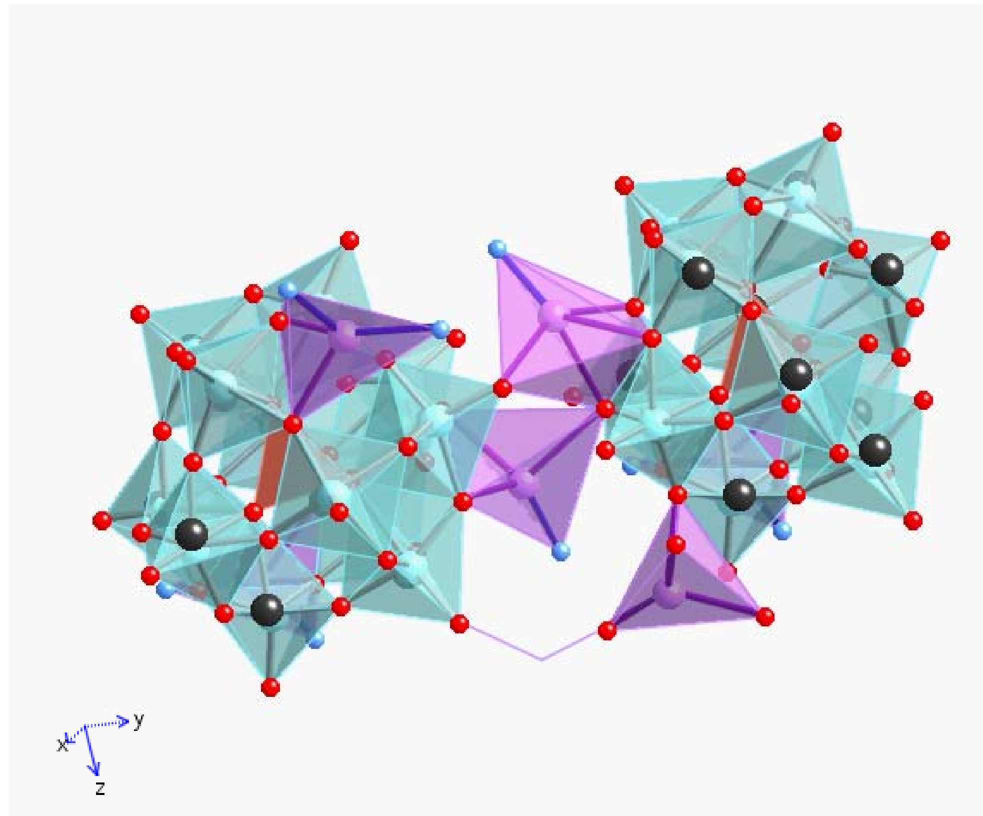


Okun, N. M.; Anderson, T. M.; Hill, C. L. *J. Mol. Catal. A: Chem.* **2003**, *197*, 283-290.

$Ag_5[PV_2Mo_{10}O_{40}]$

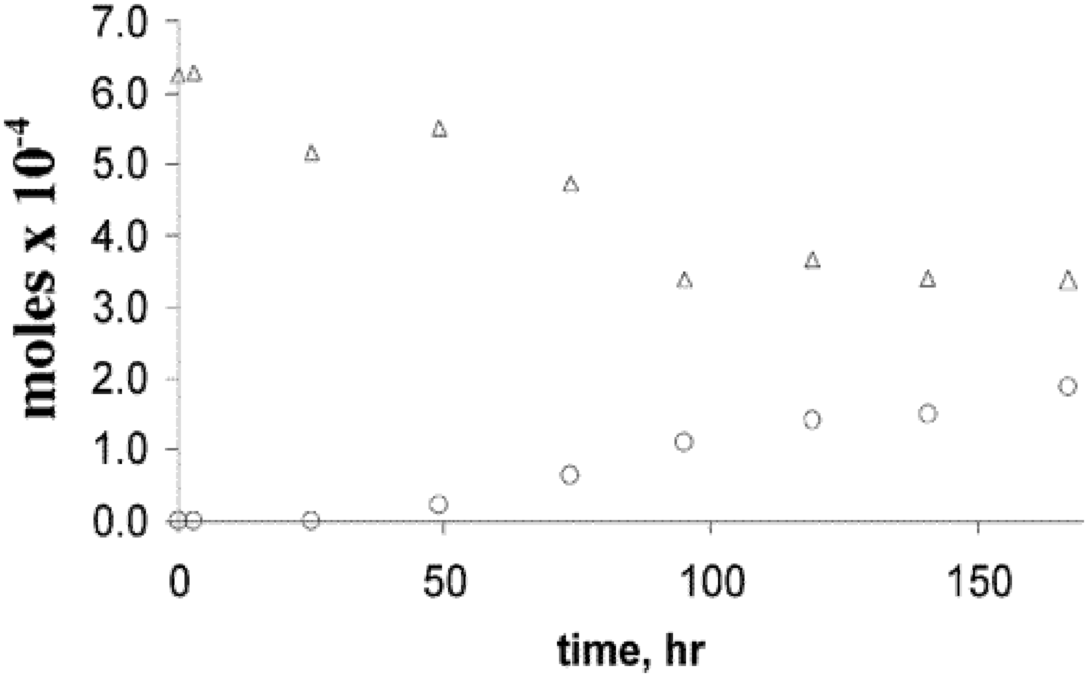
X-ray: Ag^+ bound to POM oxygens forming network.

Catalyzes air oxidation of S compounds at *R.T. and as a solid* (3 lines of evidence)



J.T. Rhule, W.A. Neiwert, K.I. Hardcastle, B.T. Do, C.L. Hill, *J. Am. Chem. Soc.* **2001**, *123*, 12101.

Oxidation of CEES to CEESO by Ag5[PV2Mo10O40] in 2,2,2-trifluoroethanol at ambient conditions (1 atm air, RT)



$[CEES]_0$ = 0.275 M

Support

ARO (Stephen Lee, Program Director)

NSF

DARPA

TDA Research

NanoScale Technologies

ONR (MDI)